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New Thermal Protection Concepts for the Next Generation Gas Turbines and Hypersonic Vehicles

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14. ABSTRACT
Thermal protection of gas turbine blades, combustors and some rocket nozzles is generally provided by thin superficial layer coatings of yttria-stabilized zirconia (YSZ). This material, deposited by either electron-beam physical vapor deposition or plasma-spraying, has exceptionally low thermal conductivity up to high temperatures but its' resistance to radiative heat transport is not known in any detail. Although oxides with still lower thermal conductivity at high temperatures than YSZ have been discovered, the mechanisms that limit radiative transport in coatings have yet to be clarified. The research performed under this contract has focused on identifying the radiative transport through current thermal barrier coatings and how this changes with long term exposure at high temperatures as well as under exposure to CMAS attack. Together with detailed modeling of combined radiative and thermal conductive heat transfer, the materials requirements and concepts for the next generation coatings have been identified.

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EXECUTIVE SUMMARY

Thermal protection of gas turbine blades, combustors and some rocket nozzles is generally provided by thin superficial layer coatings of yttria-stabilized zirconia (YSZ). This material, deposited by either electron-beam physical vapor deposition or plasma-spraying, has exceptionally low thermal conductivity up to high temperatures but its' resistance to radiative heat transport is not known in any detail. Although oxides with still lower thermal conductivity at high temperatures than YSZ have been discovered, the mechanisms that limit radiative transport in coatings have yet to be clarified. This is required before selecting materials for the next generation coatings for turbines and hypersonic vehicles. The research performed under this contract has focused on identifying the radiative transport in current coatings and how this changes with long term exposure at high temperatures as well as under exposure to CMAS attack. Together with detailed modeling of combined radiative and thermal conductive heat transfer, the materials requirements and concepts for the next generation coatings have been identified.

Existing models for heat transfer in thermal barrier coatings have usually assumed that the heat from a hot radiating gas is converted to heat at the surface of the coating and then this heat is transported by thermal conduction to the underlying metal component which is cooled by a flowing cold gas or fluid. At relatively low temperatures, the radiative heat that propagates through the coating and heats the surface of the metal coating is usually neglected. However, as gas temperatures, T, increase the radiative energy increases according to the Stefan-Boltzman equation as T^4. To establish the effect of radiative transport and heating, we have developed a continuum model for combined radiative and conductive heat transport through a coating for a wide variety of temperatures and materials properties and implemented it in Matlab. This is described in report #1, a PhD thesis that is being prepared for publication. Application of this model reveals quantitatively the role of two key materials parameters, the absorption coefficient which is a fundamental, compositionally-dependent parameter, and the optical scattering coefficient, which is microstructurally dependent parameter.

By applying the model to a series of possible microstructures designed to maximize and minimize combinations of intrinsic thermal conductivity, optical reflectivity, optical scattering, new insights have been gained into the design of coatings that will minimize heat transfer through coatings by combined radiation and conduction. Report #2. Crucial to minimizing radiative heating through a coating is a highly reflecting layer placed in the coating. Preliminary attempts to produce such reflecting coatings

using either platinum (in collaboration with H. Wadley, U. Virginia) or gold were successful but they proved to be microstructurally unstable on prolonged thermal cycling.

A formidable problem facing the development of coatings with improved resistance to the propagation of radiative heating is the determination of the optical scattering coefficient and its wavelength dependence. We have demonstrated that it can be obtained from measurements of the diffuse optical reflectance using standard diffuse scattering analyzers. This is described in report #3 and measurements as a function of wavelength and as a function of thermal cycling are presented. This work is now being extended and applied to a variety of EB-PVD coatings in collaboration with GE Aviation (B. Hazel). From this collaboration, as well as our own work, we have found that the diffuse reflectance correlates well with the coating density obtained by physical means, suggesting that the technique has the potential for non-contact evaluation of coatings, for instance, as a quality tool after TBC deposition. Furthermore, there appears to be a direct correlation between the spectral optical diffuse reflectance and the thermal diffusivity and thermal conductivity of the coatings we have examined. This is described in report #4.

As part of our investigation of the factors that affect the optical diffuse scattering, we performed a series of measurements of EB-PVD coatings of different thicknesses and with the gaps and pores infiltrated with materials having different refractive indices. The essential idea being to decrease the optical scattering that occurs as a result of the refractive index mismatch between the 7YSZ material and the gaps and pores. Infiltration with an epoxy that has a very similar refractive index to that of CMAS revealed that the optical scattering coefficient decreased significantly indicating that radiative heating would propagate further into a CMAS penetrated EB-PVD, causing an increase in bond-coat temperature. This finding is consistent with experiments we had earlier performed on heat transfer in CMAS penetrated EB-PVD. Report #5. In this work, the optical properties of CMAS were determined and a means of penetrating a EB-PVD coating perfected. Then, by using a novel time-dependent method, the thermal and radiative contributions to the heat transport through the coating was determined before and after CMAS penetration.

In parallel, the identification of oxides with low thermal conductivity was pursued and several with lower thermal conductivity than 7YSZ were found. This work, as well as the methodology developed for searching for low conductivity oxides, is described in reports # 6-8. In collaboration with colleagues at the National Institute for Materials Science in Japan, we made detailed measurements of the optical properties of tetragonal YSZ. The results of this work, in report #9, provides essential data required for modeling radiative heat transport in 7YSZ coatings. In report #10, we describe a number of non-

contact methods investigated under this contract for measuring the temperature of 7YSZ thermal barrier coatings and discuss a number of the advantages and disadvantages.

Again in parallel with main trust of the contract, we discovered that the existing method of determining thermal conductivity of low conductivity oxides and coatings is fraught with measurement uncertainty. For this reason, the commonly used thermal flash test was re-examined and new, numerically-based data reduction methods developed for extracting thermal diffusivity from the thermal flash signal. (Reports #11 and #12). Report #13 describes a new method for determining thermal diffusivity of coatings on oxidized bond-coats that takes advantages of the luminescence signal from the underlying oxide scale.

Finally, reports #14-16 describe additional research activities related to understanding the thermal cyclic life of current 7YSZ EB-PVD coatings.

As a result of our findings during the course of this contract, we are now in position to describe the requirements to minimize radiative transport in the next generation coating materials. First and foremost, the optical scattering coefficient at the wavelengths of maximum emissivity must be as large as possible. It is likely that this can be achieved by mixing micron-sized porosity and a high volume fraction of sub-micron, transparent second phases into the coating materials. The second requirement is that the coating material does not have either molecular or electronic absorption bands over the same wavelength range. Preferably, any absorption bands are well into the mid-to-far infra-red.

REPORTS OF WORK SUPPORTED UNDER CONTRACT N00014-03-I-0191

Report 1. **Heat Transport Through Thermal Barrier Coatings**, L. G. Chen, PhD Thesis (2008). To be published.

Report 2. **Design Guidelines for Minimizing Radiative Heat Transport Through Thermal Barrier Coatings**, A. M. Limarga, L. G. Chen and D. R. Clarke, to be submitted.

Report 3. **Characterization of EB-PVD Thermal Barrier Coatings by Diffuse Optical Reflectance**, A. Limarga and D. R. Clarke, International Journal of Applied Ceramic Technology, In press, 2009.

Report 4. **Evolution of Thermal Properties of EB-PVD 7YSZ Thermal Barrier Coatings with Thermal Cycling**, T. Kakuda, A. M. Limarga, T. D. Bennett and D. R. Clarke, Acta Materialia, **57** 2583-2491 (2009).

Report 5. **Effect of CMAS Infiltration on Radiative Transport Through an EB-PVD Thermal Barrier Coating**, Li Li and D. R. Clarke, International Journal of Applied Ceramic Technology, **5** 278-288 (2008).

Report 6. **Materials Selection Guidelines for Low Thermal Conductivity Thermal Barrier Coatings**, D. R. Clarke, Surface and Coating Technology, **163-164** 67-74 (2003).

Report 7. **Low Thermal Conductivity Materials for Thermal Barrier Coatings**, D. R. Clarke and S. R. Phillpot, Materials Today, **June** 22-29 (2005).

Report 8. **The Thermal Conductivity of Yttria-Stabilized Zirconia-Hafnia Solid Solutions**, M. R. Winter and D. R. Clarke, Acta Materialia, **54** 5051-5059 (2006).

Report 9. **Temperature Dependent Optical Reflectivity of Tetragonal-Prime Yttria-Stabilized Zirconia**, J. A. Nychka, T. Naganuma, M. R. Winter, Y. Kagawa and D. R. Clarke, Journal of the American Ceramic Society, **89** [3] 908-913 (2006).

Report 10. **Noncontact Methods for Measuring Thermal Barrier Coating Temperatures**, M. M. Gentleman, V. Lughi. J. A. Nychka and D. R. Clarke, International Journal of Applied Ceramic Technology, **3** [2] 105-112 (2006)

Report 11. **A Numerical Solution Based Parameter Estimation Method for Thermal Flash Diffusivity Measurements**, L. G. Chen and D. R. Clarke, Journal of Computational Materials Science, **45** 342-348 (2009).

Report 12. **A New Data Reduction Method of Pulse Diffusivity Measurements on Layered Materials**, L. G. Chen, A. M. Limarga and D. R. Clarke, Computational Materials Science. In press.

Report 13. **Optical Measurement of the Thermal Diffusivity of Intact Thermal Barrier Coatings**, B. Heeg and D. R. Clarke, Journal of Applied Physics, **104** 113119 (2008).

Report 14. **The Effect of Oxidation Pre-Treatment on the Cyclic Life of EB-PVD Thermal Barrier Coatings with Platinum-aluminide Bond Coats**, V. K. Tolpygo and D. R. Clarke, Surface and Coatings Technology, **200** 1276-1281 (2005).

Report 15. **Non-destructive Thermal Barrier Coating (TBC) Damage Assessment Using Laser-induced Luminescence and Infrared Radiometry**, B. Heeg and D. R. Clarke, Surface and Coatings Technology, **200** 1298-1302 (2005).

Report 16. **Piezospectroscopic Coefficients of Tetragonal-Prime Yttria Stabilized Zirconia**, A. M. Limarga and D. R. Clarke, Journal of the American Ceramic Society, **90** [4] 1272-1275 (2007).